March 4, 1969 C. E. JAHNIG ETAL 3,431,197

FLUID COKING USING EXTRANEOUS SEED COKE

Filed Aug. 5, 1966

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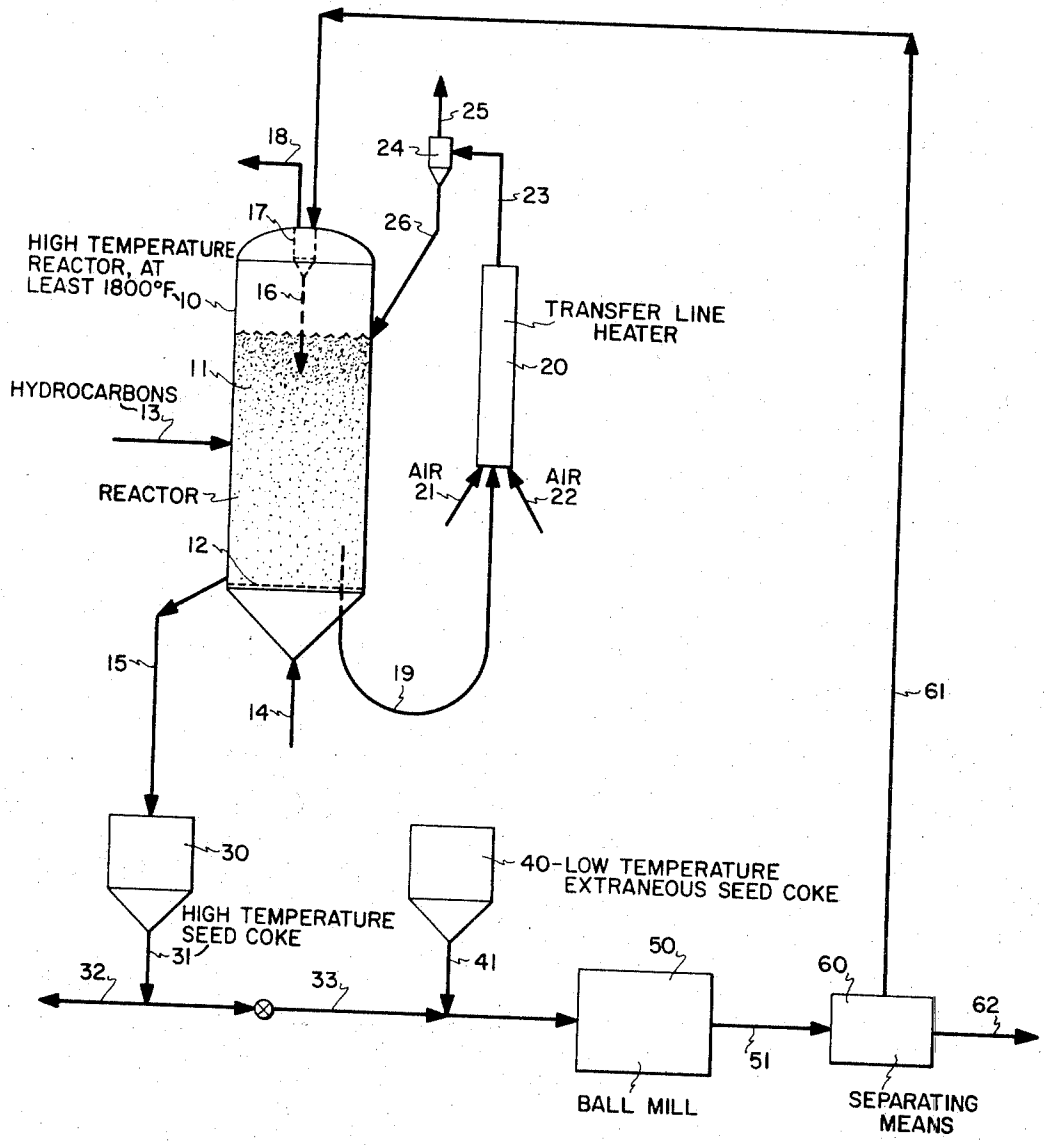


FIGURE 1

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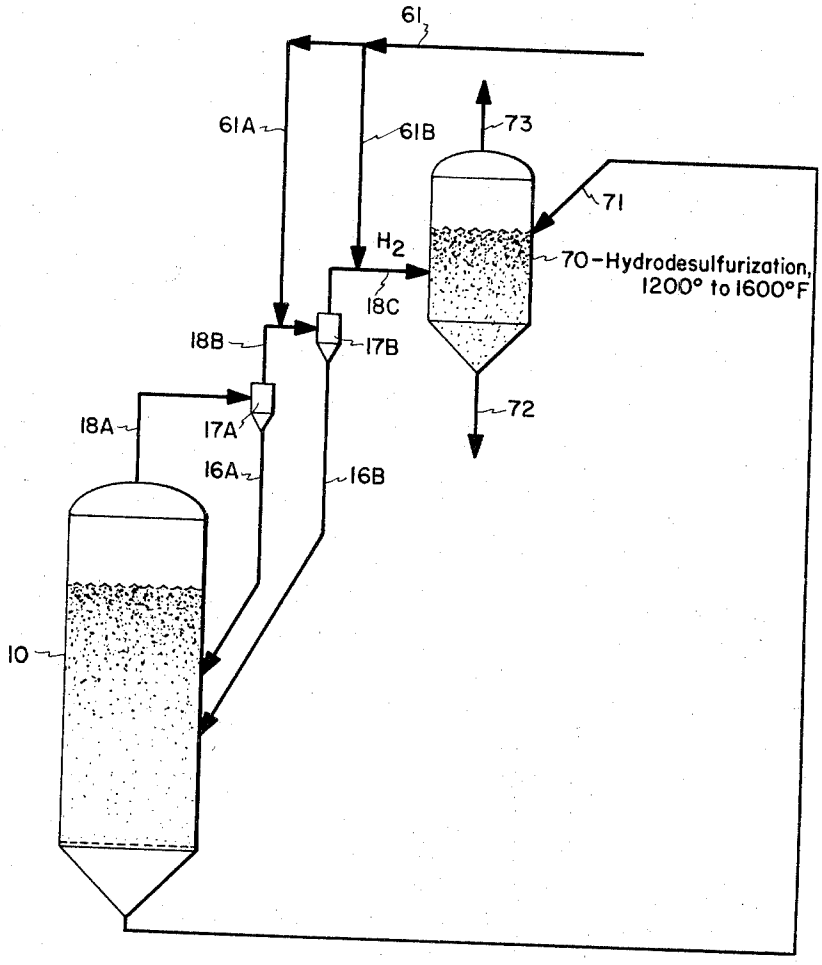


FIGURE 2

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FLUID COKING USING EXTRANEOUS SEED COKE

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Int. Cl. C10g 9/32; C10b 55/10

This invention relates to the art of producing pyrolytic coke, especially to an improved process for thermally cracking hydrocarbons at relatively high temperature by contact with particulate, relatively soft coke serving as nuclei for the formation of larger coke particles. In particular, it relates to an improved method for seeding high temperature coking reactions.

It is well known to thermally crack hydrocarbons, particularly high carbon content hydrocarbons, e.g., heavy oils, pitch, tar, residua, and the like, at temperatures ranging from about 1800° F., and higher, to about 3000° F. In such reactions, a vaporous or gaseous conversion product consisting essentially of hydrogen is produced and solid coke is formed. It is also known to thermally crack hydrocarbons below about 1800° F., especially below about 1400° F., to produce coke, but the vaporous conversion product, which is generally suitable as motor fuel, is rich in lower molecular weight hydrocarbons, including saturated and unsaturated compounds. The coke produced in these processes, generally referred to as high temperature and low temperature coking processes, respectively, differs markedly one product from the other. Thus, in the high temperature coking process, inter alia, the coke is pyrolytic in character and is formed by vapor phase deposition and liberation of free radicals at the time of cracking. On the other hand, in low temperature coking, the coke is formed by liquid phase deposition and polymerization of low molecular unsaturated hydrocarbons.

In a coking process, fluid bed reactors are generally employed. The equipment required to operate a fluid bed process includes, primarily, two vessels, a reactor and an auxiliary heater, these being interconnected and communicated one with the other via line and risers so that particulate coke can be circulated between the reactor and heater.

The reactor contains particulate coke solids in a state of dense phase fluidization, i.e., a stage wherein the solids are contacted by and suspended within a stream of ascending gases so that the total gas-solids system takes on many of the characteristics of a boiling liquid, including that of a definite "liquid" level.

A hydrocarbon, or hydrocarbon feedstock, is generally sprayed directly into the fluidized bed through a plurality of nozzles while steam or other extraneous gas, or both, is injected into the bottom of the reactor to fluidize the coke solids particles. The hydrocarbon, on contact with the hot coke particles, which act as heat carriers, immediately cracks and vaporizes to leave a carbonaceous residue on the individual coke particles. On passage of the coke particles through the heater, the temperature of the coke is elevated. On the return of the heated coke to the fluidized bed of the reactor, heat is imparted thereto to maintain the desired operating temperature. In the continuous transfer and recycle of the coke, layer upon layer of coke is deposited on the individual particles and, as a result, the coke particles, generally spherical in shape, grow by aggregation or formation of distinct "onion-skin" layers.

In low temperature coking, the heating vessel is generally a fluid bed type, with air blown through a bed of

circulating coke. However, in high temperature coking, this type heater is inefficient and a transfer line system is preferred to provide short contact time between coke and combustion gases.

In general, it is necessary to continuously supply "seed coke" to the fluidized bed of the reactor while coarser particles are continuously withdrawn as coke product. Thus, fine coke particles, or seed, are returned to serve as nuclei for the production of coarser particles, and the coarser particles are continuously discharged in the net coke production. Where coke per se is the desired product, the presence of extraneous substances is undesirable, if not intolerable, and hence seed coke is generally provided by grinding part of the product coke and returning it to the reactor.

In the production of high temperature coke it has thus been found essential to grind part of the net coke product, e.g., by jet attrition, ball milling, etc., to provide a very fine particle size coke. For one thing, there is a deficiency of very fine coke particles of the sizes required as seed because the extreme hardness of the coke prevents significant fines production within the process by attrition, as is the practice in conventional low temperature coking. Unfortunately, moreover, it is extremely difficult to grind the coke product and the time required for grinding is considerably increased. In fact, to grind such coke, far more power is required to produce seed of similar size and particle size distribution as is required, e.g., in grinding conventional delayed or fluid cokes, where grinding is necessary. Moreover, steam, which is used in the reactor for attrition in low temperature coking, can not be tolerated in a high temperature process. This is obviously disadvantageous, resulting in increased costs of production, as well as additional costs for adequate equipment.

In view of these and other difficulties, it is accordingly the primary object of the present invention to obviate these and other disadvantages. In particular, it is an object to provide an improved process for producing seed coke, and for seeding high temperature fluid coking reactions. More particularly, it is an object to provide a process which will substantially lessen, and in certain cases virtually eliminate, the normally stringent grinding operation necessary for preparation of high temperature seed coke. A further object is to provide a process for upgrading low quality coke product, while simultaneously providing improvements in processability.

These and other objects are achieved in accordance with the present invention, which contemplates the use of low temperature seed coke, for example, from conventional fluid or delayed coking of heavy vacuum residuum, as nuclei or seed for charging into a high temperature fluidized reaction for formation of high temperature coke. In particular, particulate coke from a fluidized reaction conducted at temperatures ranging from about 800° F. to about 1400° F. and preferably from about 900° F. to about 1100° F., in particle size ranging from about 40 mesh to about 400 mesh, and preferably from about 80 mesh to about 200 mesh (Taylor series) can be charged into the fluidized bed of a high temperature coke process as seed and the final coke product produced therefrom will be of unusually high quality. In fact, even when the original low temperature seed coke is of low quality, e.g., the coke has not been calcined, a high quality coke product will result from the process.

Not only can the quality of low temperature coke be upgraded, but such coke is more easily processable and seed can be more readily formed from the low temperature coke, especially before it has been calcined. In fact, less than about one-half as much power, and generally as little as one-fourth, or less, power is required to there-

by produce low temperature seed coke as is required to grind and produce high temperature seed coke of similar size and corresponding particle size distribution.

In accordance with a preferred embodiment of the invention, uncalcined low temperature coke, or coke containing up to about 5 to about 15 weight percent oils and other volatile matter, and containing as much as from about 2 to about 6 weight percent sulfur, can be charged directly into the fluidized bed of a high temperature coking process operating at from about 1400 to about 3000° F. In fact, this low quality, low temperature coke can be employed in amount ranging as high as about 35 percent, though preferably from about 5 percent to about 25 percent, based on the total weight of product withdrawn from the reaction. Pursuant to such procedure, high quality coke product can be produced. In another preferred embodiment, a mixture of very fine high temperature coke and low temperature coke is employed as seed. Even where the level of impurity is high, the low temperature coke can be admixed with the high temperature coke in concentration ranging as high as about 35 percent, based on the total weight of seed coke charged to the bed of the reactor.

That such results can be achieved is indeed surprising because the seed portion of the total coke product can range as high as about twenty percent, and typically from about ten to about fifteen percent, by weight, of the total coke withdrawn from the reaction. The introduction of the low temperature product, however, even where of poor quality, does not excessively degrade the final high temperature coke product, if at all. In fact, the low temperature coke apparently undergoes some desirable transformations in the process.

The invention will be better understood by reference to the following detailed description and to the accompanying drawings to which specific reference is made.

FIGURE 1 depicts a process scheme for the production and handling of seed coke, and

FIGURE 2 represents a preferred scheme wherein the seed coke is utilized as a heat carrier for providing process heat, and coke is hydrodesulfurized.

Referring to FIGURE 1, there is described an overall fluid coking process wherein is included a high temperature reactor with its auxiliary transfer line heater, and facilities for the preparation of seed coke. The vertically oriented cylindrical vessel with enclosing walls at its upper and lower ends defines a reaction vessel, or reactor **10**, operatively communicated with an auxiliary vessel **20** which provides process heat for the overall reactions, which are endothermic.

A perforated grid **12** is extended horizontally across the side walls at the bottom of reactor **10**, and across the flow path of the entering fluidizing gases to provide support for a dense phase fluidized bed **11** of particulate coke. Preheated residua or pitch is injected via line **13** into the fluidized bed **11** and cracked, while coke product is withdrawn from reactor **10** via line **15**. Hydrogen or other suitable carrier gas, e.g., nitrogen, gaseous hydrocarbons, and the like, can be injected into the bottom of reactor **10** via, e.g., a plurality of nozzles represented by line **14** to fluidize or aid in the fluidization if desired.

Effluent gases from the thermal cracking reaction are passed from the top of reactor **10** via a cyclone separator **17**, or separators, through line **18**. Entrained coke particles are separated from separator **17** and returned to fluidized bed **11** through a dipleg **16**.

Coke solid particles are removed from the bottom of bed **11** of reactor **10** along with some of the process gas, if desired, and passed via line **19**, in dilute phase, through the transfer line heater **20**, into which a combustible gas and an oxygen-containing gas, e.g. air, are injected via lines **21**, **22** and burned to provide heat. After heating, the particles are thence returned via line **23** to a cyclone separator **24** which separates the flue gases, which are evolved therefrom via line **25**, while the solids coke particles are returned to the fluidized bed **11** of reactor **10** via dipleg **26**. In passage through the heater **20**, the temperature of the coke particles is elevated sufficiently to provide and maintain the desired process heat in fluidized bed **11**.

Particulate coke, ranging generally in size from about 200 mesh to 20 mesh (74 to 800 microns) and having an average particle size of about 100 mesh (150 microns) is withdrawn from the bottom of reactor **10** via line **15** and passed via line **27** to the hopper **30**. Coke is withdrawn from hopper **30** via line **31**, the net coke product being taken therefrom via line **32** while another portion, to be used for preparation of seed coke, is taken therefrom via valved line **33**, if desired. Thus, in some instances it is desirable to return a mixture of high temperature seed coke and low temperature seed coke to reactor **10**.

Preferably, however, seed coke from an extraneous process, i.e., a low temperature fluidized coke process, is provided in hopper **40**. This coke is withdrawn from hopper **40** via line **41** and passed through line **33** to suitable grinding apparatus, e.g., a ball mill **50**. Within the ball mill **50** low temperature fluid coke, with some high temperature fluid coke, if desired, is ground to provide fines containing particles of size distribution ranging from less than 400 to about 40 mesh, and preferably from about 200 to about 80 mesh. These fines are passed via line **51** into size separating means **60**, e.g., a sieve, screen, or the like, to concentrate the particles of desirable size. Undersize fines are taken as product via line **62**. Seed particles are then returned via line **61** to fluidized bed **11** of reactor **10**.

A desirable process scheme is also shown by reference to FIGURE 2. In this figure, parts corresponding generally to similar parts of FIGURE 1 are numbered the same, the letter A designating specifically a substitute member and the letters B and C additional generally similar members. In the figure is thus shown a reactor **10** provided with a pair of external cyclone separators **17A**, **17B** arranged in series, reactor off-gas flowing into the first cyclone separator **17A** via line **18A**, and into the second cyclone separator via line **18B**. Solids are returned from the cyclone separators **17A**, **17B** to the reactor **10** via diplegs **16A**, **16B**.

In accordance with a desirable method of introduction, the seed coke in line **61** is fed to the inlet line **18B** of cyclone separator **17B** to quench the gaseous product from the reactor, while simultaneously the seed coke is preheated. Preferably, however, the seed coke is introduced to treating vessel **70** via lines **61B**, **18C**. In some instances the first cyclone separator **17A** can be omitted, e.g., where reactor **10** operates at a velocity such that entrainment of solids is relatively low. In preparation of the seed coke, the particles which are too finely ground—viz., the flour—can be taken as a separate product via line **62**.

By use of low temperature fluidized coke as seed for the high temperature reaction, the quality of the low temperature product is upgraded. Thus, despite the poor characteristics of the uncalcined low temperature coke, the latter apparently undergoes a marked change when subjected to treatment in the high temperature coking process. Thus, the low temperature product is converted into a suitable grade of high temperature coke product. Though the reason for this change in character is not known, it is believed that the low temperature coke product is calcined when subjected to the high temperature coking operation, or the poor characteristics of the low temperature coke product is "masked" at least in part by the deposition of the high temperature coke thereupon, or both. It is thought that the low temperature extraneous coke becomes porous when heated, and these pores are then filled by coke deposited in the high temperature reactor. In any event, the end product is virtually equivalent

to high temperature coke formed from high temperature coke seed, when used in electrodes.

It has thus been found that the difficult problem of grinding high temperature seed coke can be greatly reduced, or can be, in some cases, virtually eliminated. The use of the present technique in seeding high temperature coking operations is quite significant for typically up to about 20 weight percent, and higher, of the coke product must be ground and returned to the reactor. Moreover, low temperature coke product used as seed, though of poor quality, can even be upgraded into a product which is substantially high temperature coke. Thus, uncalcined low temperature fluidized coke containing up to about 15 percent volatile matter, and even as high as about two to about 6 percent sulfur, can be used to replace from about 15 to about 35 percent of the high temperature coke which is normally used for seed in the process. Thus, in effect, the yield of high quality, high temperature coke in a given process can be increased by this amount at the expense of a low quality extraneous raw material in a given process.

An unusual benefit can be obtained in connection with the combined treating steps of this invention. Coke can be desulfurized by treating with hydrogen at from about 1200 to about 1600° F. for ½ to several hours. This upgrading can be carried out conveniently by using treating vessel **70**, wherein coke is added via line **71** and contacted with hot hydrogen containing gas introduced via line **18**C. The latter gas supplies part or all of the heat required, and at the same time part of the required cooling of this gas is accomplished. Coke feed may be from high or low temperature coking, or both. Treated product coke is withdrawn via line **72**, while off-gas from line **73** is further treated for sulfur recovery.

It is apparent that the invention is subject to some changes and modifications without departing the spirit and scope of the invention. Hence, the claims should be construed within the spirit and scope of the foregoing disclosure.

Having described the invention, what is claimed is:

1. In a coking process for forming larger coke particles from smaller seed coke particles which includes the steps of (a) fluidizing and forming a bed of particulate coke within a high temperature reaction zone, (b) withdrawing particulate coke from said reaction zone and passing same through a heating zone to elevate the temperature of the coke, thence returning the heated coke to the reaction zone to supply process heat while maintaining the fluidized bed at a temperature of at least about 1800° F., (c) contacting the particulate coke solids of the bed with a hydrocarbon to form a gaseous effluent and to deposit coke on the coke solids particles, and (d) withdrawing particulate coke from the fluidized bed of the reaction zone as product, the improvement comprising (e) transferring from an extraneous process to the fluidized bed of the reaction zone a low temperature seed coke formed at temperatures ranging from about 900° F. to about 1400° F., said coke seeds being of particle size ranging from about 325 mesh to about 40 mesh.

2. The process of claim **1** wherein the seed coke transferred to the fluidized bed of the reaction zone is a finely ground mixture of low temperature fluid coke and high temperature fluid coke.

3. The process of claim **1** wherein up to about 35 percent of impure, uncalcined low temperature coke, based on the total weight of product coke, is fed to the fluidized bed of the reaction zone.

4. The process of claim **1** wherein the low temperature seed coke is formed in a low temperature fluid bed process, is uncalcined, and contains up to about 15 percent by weight of volatile matter, from about two to about 6 percent sulfur, and is of mesh size ranging from about 300 mesh to about 40 mesh.

5. In a coking process for forming larger coke particles from smaller seed coke particles which includes the steps of (a) fluidizing and forming a bed of particulate coke within a high temperature reaction zone, (b) withdrawing particulate coke from said reaction zone and passing same through a heating zone to elevate the temperature of the coke, thence returning the heated coke to the reaction zone to supply process heat while maintaining the fluidized bed at a temperature of at least about 1800° F., (c) contacting the particulate coke solids of the bed with a hydrocarbon to form a gaseous effluent consisting essentially of hydrogen while depositing coke on the coke solids particles, and (d) withdrawing particulate coke from the fluidized bed of the reaction zone as product, the improvement comprising (e) contacting at least a portion of the coke product withdrawn from the reaction zone with hydrogen at temperatures ranging from about 1200° F. to about 1600° F. for a time sufficient to hydrodesulfurize same, (f) and thence transferring the hydrodesulfurized coke to the fluidized bed of the reaction zone.

6. The process of claim **5** wherein the hydrogen used for hydrodesulfurization of the coke is that evolved from the process.

7. The process of claim **5** wherein the coke is maintained in contact with the hydrogen for a period of at least about one-half hour.

8. The process of claim **5** wherein the coke which is hydrodesulfurized and transferred to the fluidized bed of the reaction zone is one produced in the reaction by charging a finely ground low temperature seed coke to the fluidized bed of the reaction zone.

9. The process of claim **8** wherein the seed coke initially charged to the reaction zone contains up to about 35 percent of impure, uncalcined low temperature coke, based on the total weight of the product coke.

10. The process of claim **8** wherein the seed coke which is hydrodesulfurized and initially charged to the fluidized bed of the reaction zone is a finely ground mixture of low temperature fluid coke and high temperature fluid coke.

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